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For

Contract N00014-90-J-1148

R&T Code 4132016

Dynamics Simulation of Langmuir-Blodgett Films

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Prepared for Preprints Polymer
ACS Boston
Meeting April 1990

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REPORT DOCUMENTATION PAGE

Form Approved
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2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 13	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION University of Lowell 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research, Chemistry
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry One University Avenue Lowell, MA 01854	7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000
8a. NAME OF FUNDING/SPONSORING ORGANIZATION ONR 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-90-J-1148
8c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
Dynamics Simulation of Langmuir-Blodgett Films

12. PERSONAL AUTHOR(S)
S. B. Clough, X. F. Sun, J. Kumar and S. Tripathy

13a. TYPE OF REPORT	13b. TIME COVERED FROM ____ TO ____	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT 2

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION
22a. NAME OF RESPONSIBLE INDIVIDUAL Professor Sukant Tripathy	22b. TELEPHONE (Include Area Code) 508-458-7116 / 22c. OFFICE SYMBOL

DD Form 1473, JUN 86 Previous editions are obsolete. SECURITY CLASSIFICATION OF THIS PAGE

DYNAMICS SIMULATION OF LANGMUIR-BLODGETT FILMS

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Introduction

Langmuir-Blodgett film monolayers are formed when amphiphilic molecules in solution are deposited on water surface followed by compression. During the compression, the randomly oriented molecules reorient themselves with the hydrophilic head groups on the water surface and the hydrophobic tail standing away from the water surface. The organic ultra-thin films with highly ordered layer structure, have shown a wide range of potential applications in biochemistry, microelectronics, integrated optics, microlithography, and many other fields [1]. It is very important to get a better understanding of the relationship between the properties of the films and the micro-structure, for example, the molecular conformation, packing, orientation and motion in the films. For this purpose, within the past few years, different computer simulation methods were applied on LB film monolayers, including Monte Carlo methods [2,3] and molecular dynamics simulations [4-6]. In this paper, we present the results of a molecular dynamics simulation of a fatty acid ($CH_3(CH_2)_{27}COOH$) monolayer on a water surface. This fatty acid is a preliminary model for our next study object: $CH_3(CH_2)_{15}C{\equiv}C\text{-}C{\equiv}C(CH_2)_8COOH$.

Methodology

QUANTA 2.0 (CHARMm 21), a comprehensive, integrated molecular modelling package developed by Polygen Corporation is used in the present simulation. In this calculation, the Steepest Descents method [7] is employed for energy minimization and the Verlet algorithm is employed for the dynamics simulation. The hardware employed is a GS1000 Graphics Supercomputer from Stellar Computer Inc.

The simulation starts with 169 molecules, in a 13x13 matrix, parallel to each other standing vertically on a layer of water. During the dynamics simulation, the position of the water molecules are frozen. A 15x15 molecule matrix (225 molecules) without water is also studied.

To relax the conformation and remove bad contacts, the system undergoes energy minimization at zero K. The potential energy terms concerned are:

$$E_p = E_{\text{bond length}} + E_{\text{bond angle}} + E_{\text{dihedral angle}} + E_{\text{improper torsion}} + E_{\text{electrostatic}} + E_{\text{van der waals}}$$

The energy for hydrogen bonding is included in electrostatic and van der waal terms.

The optimized system is then heated to the desired temperature, i.e. 300K, by gradually assigning random velocities to each atom. The relationship between the atom velocity, the kinetic energy and temperature of the system is:

$$E_{\text{kinetic}} = \frac{1}{2}\sum_{i=1}^{N} m_i\langle v_i^2\rangle = \frac{3}{2}Nk_BT$$

where N is the total number of atoms and m_i and v_i are the ith atom's mass and velocity, respectively; k_B is Boltzmann's constant.

When the system is heated to 300K, it undergoes a equilibration period to stabilize average temperature and structure. After the system is equilibrated, the final molecular dynamics simulation starts. The coordinates of the molecules are recorded periodically. The sets of coordinates recorded during the dynamics simulation are then analyzed to extract information about molecular packing, orientation and motion.

Results and Discussion

Water strongly limits the mobility of the molecules, especially the polar head groups. In Table I, the vertical mobility of the two end-groups of the molecules is represented by the fluctuations in height. Without water, both end-groups have similar fluctuations as shown in Table I and Fig. 1a. When water is introduced into the system, the surface formed by the polar groups (the lower curve in Fig. 1b) is more even due to their hydrophilic interaction.

During the simulation the molecules tend to adjust the intermolecular distance to reach the minimum potential energy. For closely packed systems (i.e. with smaller area per molecule), the final molecular areas of 21-22Å^2 (see Table I) are consistent with that for 'close-packed heads' phase of fatty acids monolayers [8]. For closely packed system, there is pseudohexagonal packing with defects (Fig. 2). Relatively loosely packed systems however have significantly less packing order.

Comparing Fig. 3a and 3b we can see that the center molecule, surrounded by other molecules, has low mobility and flexibility, represented by the tilt and molecular length respectively; the molecule at a corner of the molecule matrix has more mobility and flexibility. When loosely packed, there is more space around each molecule and the cohesion is weaker, therefore the molecules will have more tilt (see Table I) and stronger edge effect as shown in Fig. 4: the tilts for central molecules are less then 10° and for molecules at the matrix corner can be as high as 60°. To correct for the edge effect, simulations with periodic boundaries are being made and will be discussed.

Conclusion

Simulations of the LB films without periodic boundaries show clearly the effect of water and packing condition on the behavior of molecules in the monolayer. It is instructive to see appearance of domain boundaries and lattice defects in the simulation process as result already seen experimentally but whose origin is not well understand. The strong edge effect makes it necessary to introduce periodic boundaries in future simulations.

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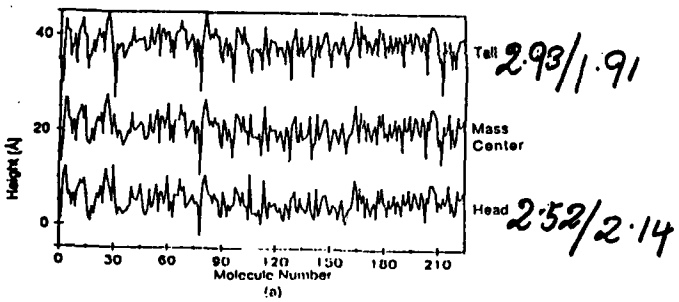
References

1. V. K. Agarwal, Physics Today, 41, 5(1988)40
2. J. Harris and S. A. Rice, J. Chem. Phys., 88(1988) 1298
3. B. Owenson and L. R. Pratt, J. Phys. Chem., 88(1984)6048
4. J. Harris and S. A. Rice, J. Chem. Phys., 89(1988)5898
5. J. Hautman and M. L. Klein, J. Chem. Phys., 91(1989)4994
6. A. Ulman et. al, Langmuir, 5(1989)1147
7. B. Broods et. al, J. of Comput. Chem. 4(1983)187
8. G. L. Gaines, Jr., *Insoluble Monolayers at Gas-Liquid Interfaces* (Interscience Publishers, New York 1966)

Table I. The height fluctuation [Å] of the end-groups, the change of molecular area [Å²/molecule] and the average tilt [°] in the dynamics simulations with and without water. The simulation time scale is pico second [ps]

Simulation	15x15 molecules without water		13x13 molecules with water	
	Molecular Area [Å²/molecule]			
Start	16	36	25	36
End	21	25	22	27
	Fluctuation In Height [Å]			
Head Group	2.52	4.18	1.14	0.86
Tail Group	2.93	4.16	3.83	3.54
	Average Tilt [°]			
First 30ps	9.37	14.65(17ps)	12.35	20.02
Last 30ps			18.44	30.00



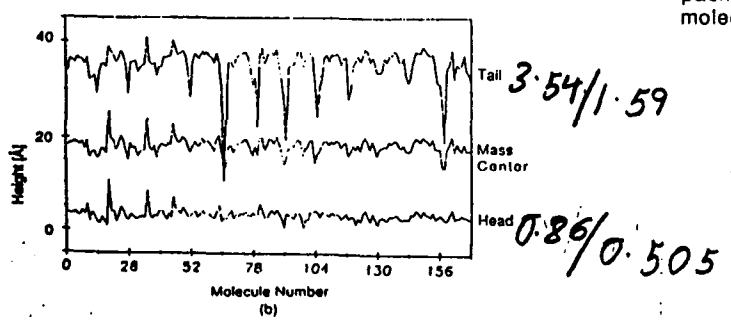


Fig. 1 The time averaged height of the mass center and the two end-groups of the molecules. (a) Without water (21 Å²/molecule). (b) With water (22Å²/molecule).

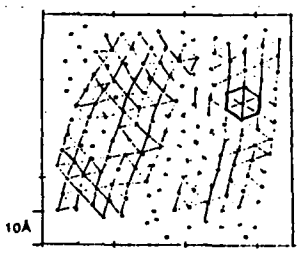


Fig. 2 The projection of average mass centers of the molecules (open circle) on a water surface with molecular area 22Å²/molecule (starting from 25Å²).

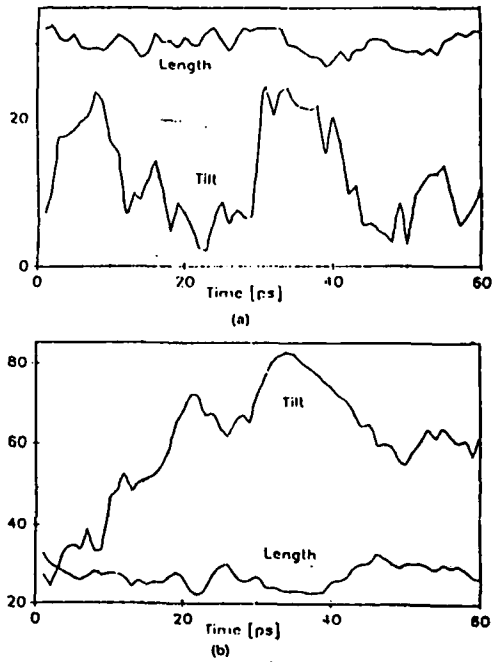


Fig. 3 The molecular length [Å] and tilt [°] as a function of dynamics simulation time(in pico seconds) for (a) a center molecule and (b) a corner molecule in a loosely packed system(27Å²/molecule).(0° tilt means the molecule is vertical to water surface).

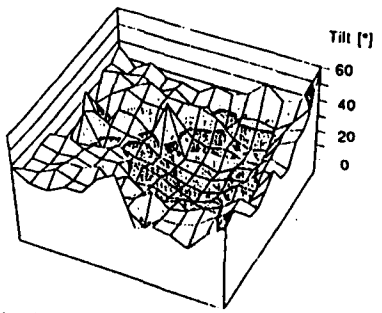


Fig. 4 The average tilt angle [°] of molecules in a loosely packed system vs. the molecule position in two dimensions with molecular area 27Å² for 30 ps simulation.

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